HF, DFT and 1MFT all have occupation and orbital, Karush–Kuhn–Tucker conditions to solve them all

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Outline

Optimization problem

$$E[\{\phi\},\{\phi^*\},\{n\}] = \sum_r n_r \langle \phi_r | \hat{h} | \phi_r \rangle + W[\{\phi\},\{n\}]$$

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$$W^{\text{1MFT}}[\{\phi\},\{\phi^*\},\{n\}] = W[\gamma]$$

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The N orbitals with the lowest orbital energy are occupied.
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Questions

How to deal with degeneracy?
Can the Aufbau-assumption mathematically be justified?

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Karush–Kuhn–Tucker conditions

Karush (1939); Kuhn and Tucker (1951)

Phase invariance

$$\gamma(\boldsymbol{x}, \boldsymbol{x}') = \sum_k n_k \phi_k(\boldsymbol{x}) \phi_k^*(\boldsymbol{x}')$$

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$$F_{kl} := \int \mathrm{d}\boldsymbol{x}\, \frac{\partial F}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x})$$

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$$F_{kl} := \int \mathrm{d}\mathbf{x}\, \frac{\partial F}{\partial \phi_k(\mathbf{x})} \phi_l(\mathbf{x}) \qquad \Rightarrow \qquad F_{kk}^\dagger - F_{kk} = 0$$

A student's adventure: part 1

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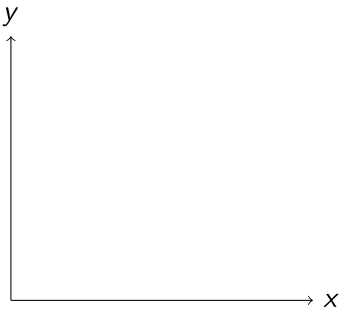

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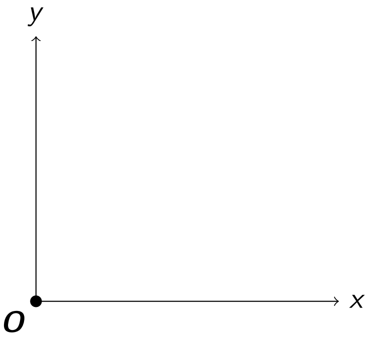

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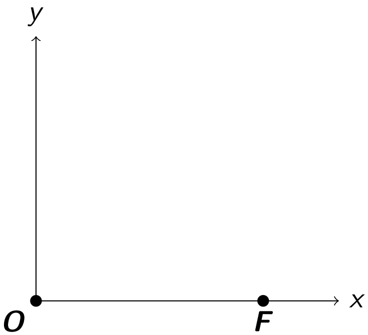

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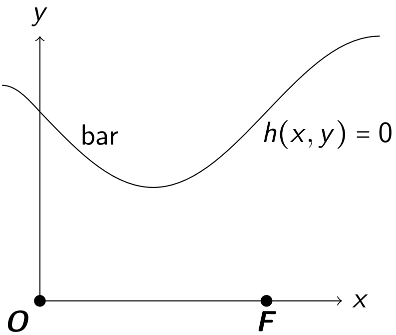
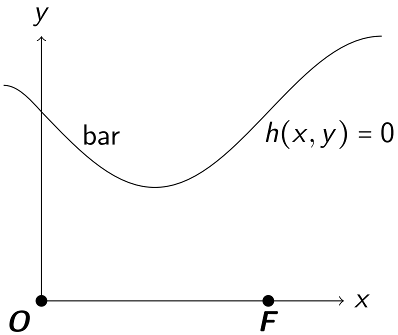


A student's adventure: part 1

$$f = d_{OB} + d_{BF}$$



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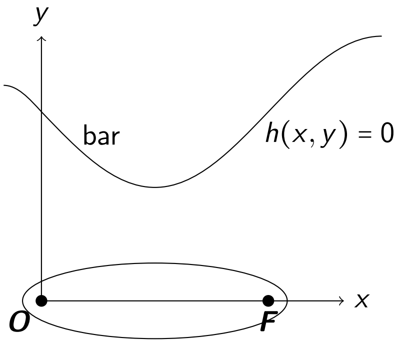

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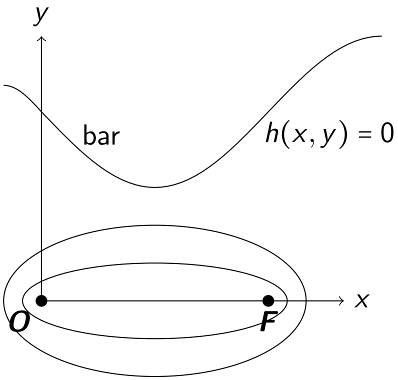

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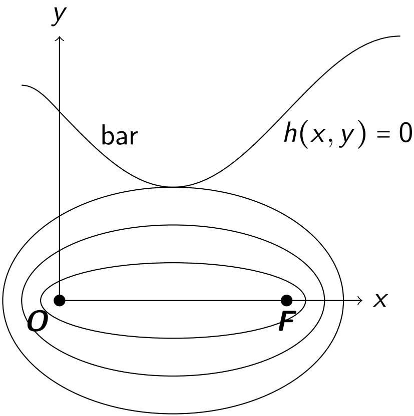

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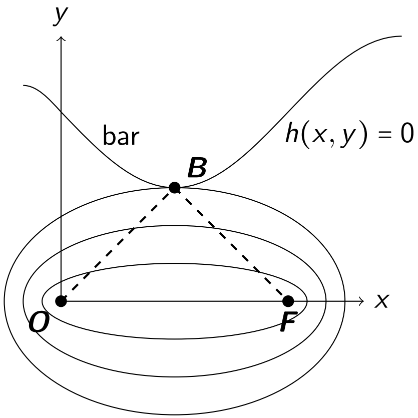

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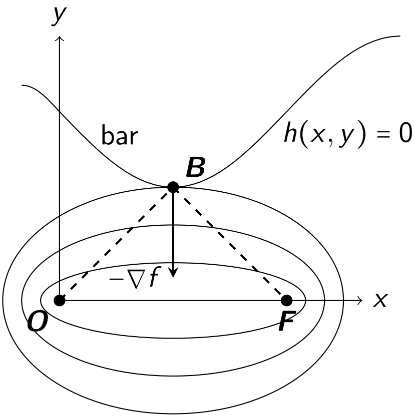

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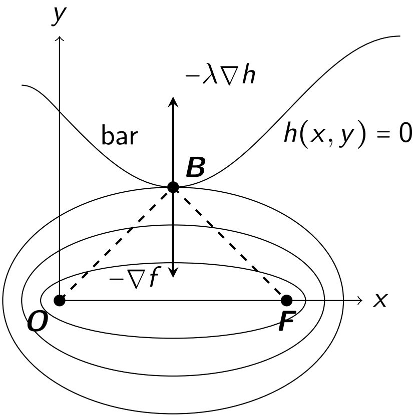

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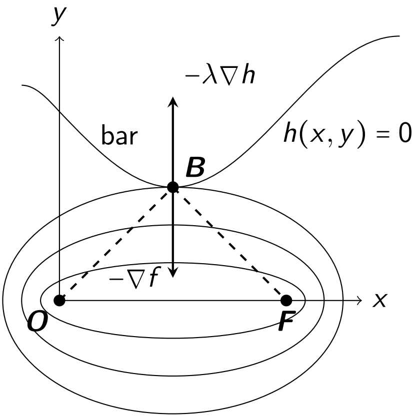
$$f = d_{OB} + d_{BF}$$

Force balance

$$\nabla f + \lambda \nabla h = \mathbf{0}$$



Generalisation

$$\begin{aligned} &\min_{\boldsymbol{x}\in\mathbb{R}^n} && f(\boldsymbol{x}) \\ &\text{subject to} && h_j(\boldsymbol{x}) = 0 \qquad \text{for } j = 1, \ldots, l \end{aligned}$$

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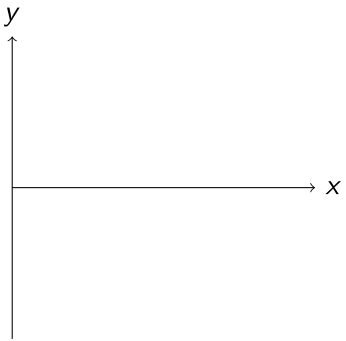

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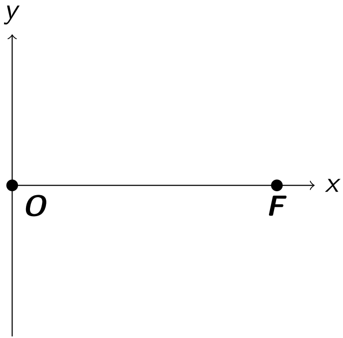

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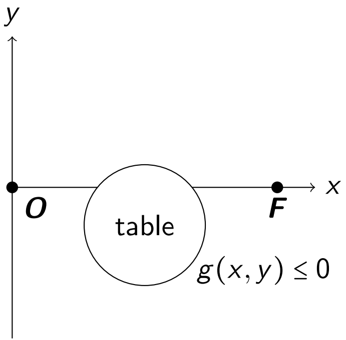

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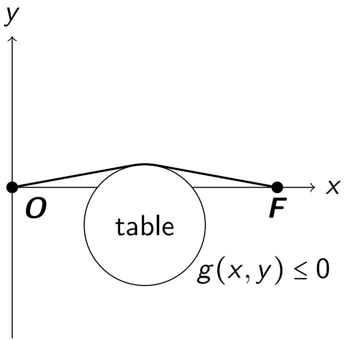

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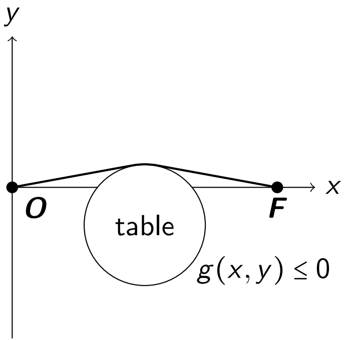
   $(g(x,y) \leq 0)$



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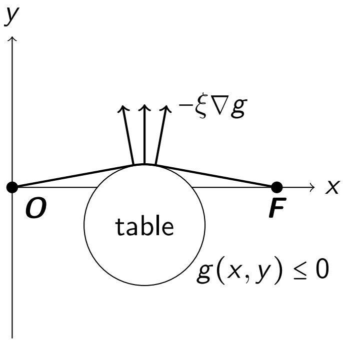

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Combined into

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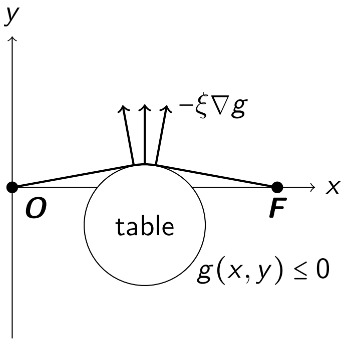

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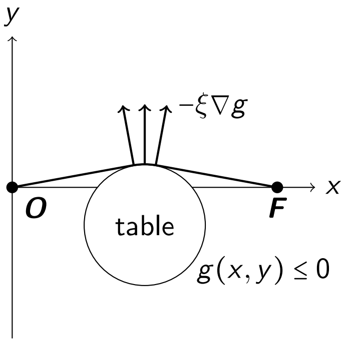

Lagrangian

$$
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\min_{\boldsymbol{x}\in\mathbb{R}^N} \quad & f(\boldsymbol{x}) & & \\
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Lagrangian:

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Karush-Kuhn-Tucker (KKT) conditions

Dual feasibility

$$\nabla_{\boldsymbol{x}} L(\boldsymbol{x}, \boldsymbol{\xi}, \boldsymbol{\lambda}) = \nabla f(\boldsymbol{x}) + \sum_{i=1}^{m} \xi_i \nabla g_i(\boldsymbol{x}) + \sum_{j=1}^{l} \lambda_j \nabla h_j(\boldsymbol{x}) = \mathbf{0},$$

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Minimize $f(x, y) = -x$

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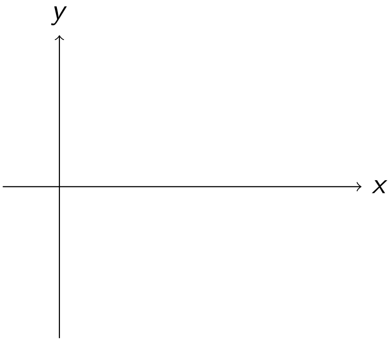

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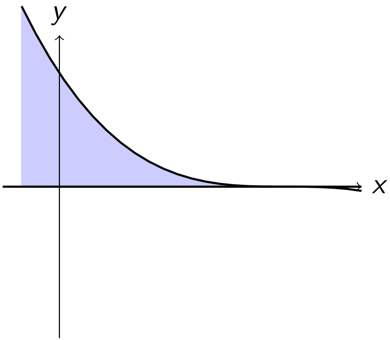

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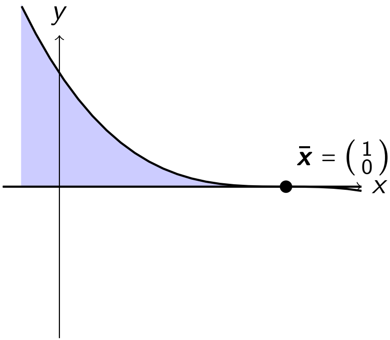

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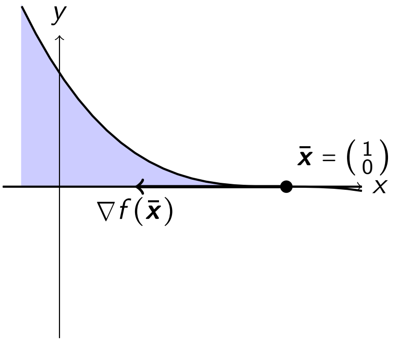
$$y - (1 - x)^3 = g_1(x, y) \leq 0$$
$$-y = g_2(x, y) \leq 0$$



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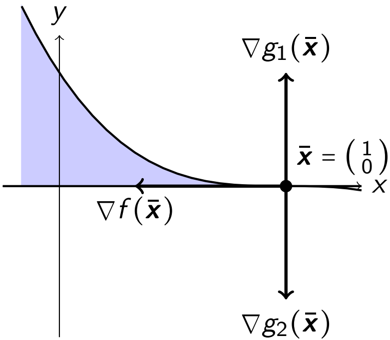

Constraint qualification

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other CQs Cottle's CQ, Zangwill's CQ, Kuhn–Tucker's CQ, Slater's CQ, Abadie's CQ, etc.

Energy Lagrangian

$$\Omega[\{\phi\},\{\xi^*\},\boldsymbol{n} \qquad\qquad] = E[\{\phi\},\{\xi^*\},\{n\}]$$

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Energy Lagrangian

$$\Omega[\{\phi\},\{\xi^*\},\boldsymbol{n},\boldsymbol{\lambda} \qquad] = E[\{\phi\},\{\xi^*\},\{n\}] - \sum_{rs}\lambda_{sr}\big(\langle\xi_r|\phi_s\rangle - \delta_{rs}\big)$$

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Energy Lagrangian

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$n_r \geq 0$

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$$E_{kl}^\dagger - E_{kl} = 0 \qquad E_{kl} := \int \mathrm{d}\boldsymbol{x}\, \frac{\partial E}{\partial\phi_k(\boldsymbol{x})}\phi_l(\boldsymbol{x})$$

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$$0 = \frac{\partial\Omega}{\partial n_k} = \frac{\partial E}{\partial n_k} - \epsilon - \epsilon^0_k + \epsilon^1_k$$

Energy Lagrangian

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$$\frac{\partial E}{\partial n_k} = \epsilon_k \qquad\qquad \epsilon_k := \epsilon + \epsilon_k^0 - \epsilon_k^1$$

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$$\epsilon_k^1 \geq 0 \qquad \epsilon_k^1 (1 - n_k) = 0$$

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n_k	ϵ_k^0	ϵ_k^1	ϵ_k

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n_k	ϵ_k^0	ϵ_k^1	ϵ_k
$0 < n_k < 1$	0	0	$\epsilon_k = \epsilon$

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$0 < n_k < 1$	0	0	$\epsilon_k = \epsilon$
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$n_k = 1$	0	$\epsilon_k^1 \geq 0$	$\epsilon_k \leq \epsilon$

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n_k	ϵ_k^0	ϵ_k^1	ϵ_k	
$0 < n_k < 1$	0	0	$\epsilon_k = \epsilon$	fractional
$n_k = 0$	$\epsilon_k^0 \geq 0$	0	$\epsilon_k \geq \epsilon$	virtual
$n_k = 1$	0	$\epsilon_k^1 \geq 0$	$\epsilon_k \leq \epsilon$	occupied

Is ϵ_k an orbital energy?

$$\epsilon_l \phi_l(\boldsymbol{x}) = \hat{h}^{\text{eff}}[\{\phi\}, \{n\}]\phi_l(\boldsymbol{x})$$

Is ϵ_k an orbital energy?

$$\epsilon_l \phi_l(\boldsymbol{x}) = \hat{h}^{\text{eff}}[\{\phi\},\{n\}]\phi_l(\boldsymbol{x}) = \big(\hat{h} + \hat{v}^{\text{eff}}[\{\phi\},\{n\}]\big)\phi_l(\boldsymbol{x})$$

Is ϵ_k an orbital energy?

$$\epsilon_k \delta_{kl} = h_{kl} + v^{\text{eff}}_{kl}[\{\phi\},\{n\}]$$

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$$E_{kl} = n_k h_{kl} + W_{kl} \quad \Rightarrow \quad E^\dagger_{kl} = n_l h_{kl} + W^\dagger_{kl}$$

$$E^\dagger_{kl} - E_{kl} = (n_l - n_k) h_{kl} + \left(W^\dagger_{kl} - W_{kl}\right) = 0 \quad \forall_{k \neq l}$$

Is ϵ_k an orbital energy?

$$\epsilon_k \delta_{kl} = h_{kl} + v^{\text{eff}}_{kl}\big[\{\phi\}, \{n\}\big]$$

$$0 = h_{kl} + \frac{W^{\dagger}_{kl} - W_{kl}}{n_l - n_k} \qquad \forall_{k \neq l}$$

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$$v^{\text{eff}}[\{\phi\},\{n\}] := \begin{cases} \dfrac{W^\dagger_{kl} - W_{kl}}{n_l - n_k} & \text{for } k \neq l \\ \dfrac{\partial W}{\partial n_k} & \text{for } k = l \end{cases}$$

Derivation of the Fock potential

$$W^{\mathrm{HF}}[\{\phi\},\{n\}] = \frac{1}{2}\sum_{rs} n_r n_s \langle rs|rs\rangle - \frac{1}{2}\sum_{rs} n_r n_s \langle rs|sr\rangle$$

Derivation of the Fock potential

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$$\langle kl|ba\rangle := \int \mathrm{d}\boldsymbol{x}_1 \int \mathrm{d}\boldsymbol{x}_2\, \phi_k^*(\boldsymbol{x}_1)\phi_l^*(\boldsymbol{x}_2) w(\boldsymbol{x},\boldsymbol{x}')\phi_b(\boldsymbol{x}_1)\phi_a(\boldsymbol{x}_2)$$

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Derivation of the Fock potential

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$$W_{kl}^{\mathrm{HF}} = \int \mathrm{d}\boldsymbol{x}\, \frac{\partial W^{\mathrm{HF}}}{\partial \phi_k(\boldsymbol{x})}\phi_l(\boldsymbol{x}) = n_k \sum_r n_r \langle kr|lr\rangle - n_k \sum_r n_r \langle kr|rl\rangle$$

Derivation of the Fock potential

$$W^{\mathrm{HF}}[\{\phi\},\{n\}] = \frac{1}{2}\sum_{rs} n_r n_s \langle rs|rs\rangle - \frac{1}{2}\sum_{rs} n_r n_s \langle rs|sr\rangle$$

$$\langle kl|ba\rangle := \int \mathrm{d}\boldsymbol{x}_1 \int \mathrm{d}\boldsymbol{x}_2\, \phi_k^*(\boldsymbol{x}_1)\phi_l^*(\boldsymbol{x}_2) w(\boldsymbol{x},\boldsymbol{x}')\phi_b(\boldsymbol{x}_1)\phi_a(\boldsymbol{x}_2)$$

$$W_{kl}^{\mathrm{HF}} = \int \mathrm{d}\boldsymbol{x}\, \frac{\partial W^{\mathrm{HF}}}{\partial \phi_k(\boldsymbol{x})}\phi_l(\boldsymbol{x}) = n_k \sum_r n_r \big(\langle kr|lr\rangle - \langle kr|rl\rangle\big)$$

Derivation of the Fock potential

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$$W_{kl}^{\mathrm{HF}\dagger}$$

Derivation of the Fock potential

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$$\langle kl|ba\rangle := \int \mathrm{d}\boldsymbol{x}_1 \int \mathrm{d}\boldsymbol{x}_2\, \phi_k^*(\boldsymbol{x}_1)\phi_l^*(\boldsymbol{x}_2) w(\boldsymbol{x},\boldsymbol{x}')\phi_b(\boldsymbol{x}_1)\phi_a(\boldsymbol{x}_2)$$

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$$W_{kl}^{\mathrm{HF}\dagger} = W_{lk}^{\mathrm{HF}*}$$

Derivation of the Fock potential

$$W^{\mathrm{HF}}[\{\phi\},\{n\}] = \frac{1}{2}\sum_{rs} n_r n_s \langle rs|rs\rangle - \frac{1}{2}\sum_{rs} n_r n_s \langle rs|sr\rangle$$

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$$W_{kl}^{\mathrm{HF}} = \int \mathrm{d}\boldsymbol{x}\, \frac{\partial W^{\mathrm{HF}}}{\partial \phi_k(\boldsymbol{x})}\phi_l(\boldsymbol{x}) = n_k \sum_r n_r\big(\langle kr|lr\rangle - \langle kr|rl\rangle\big)$$

$$W_{kl}^{\mathrm{HF}\dagger} = W_{lk}^{\mathrm{HF}*} = n_l \sum_r n_r\big(\langle lr|kr\rangle^* - \langle lr|rk\rangle^*\big)$$

Derivation of the Fock potential

$$W^{\mathrm{HF}}[\{\phi\},\{n\}] = \frac{1}{2}\sum_{rs} n_r n_s \langle rs|rs\rangle - \frac{1}{2}\sum_{rs} n_r n_s \langle rs|sr\rangle$$

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Derivation of the Fock potential

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$\forall_{k \neq l}$ $\qquad v_{kl}^{\mathrm{HF}}$

Derivation of the Fock potential

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Derivation of the Fock potential

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Derivation of the Fock potential

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$$v_{kk}^{\mathrm{HF}} = \frac{\partial W^{\mathrm{HF}}}{\partial n_k}$$

Derivation of the Fock potential

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$$\forall_{k\neq l} \qquad v_{kl}^{\mathrm{HF}} = \frac{W_{kl}^{\mathrm{HF}\dagger} - W_{kl}^{\mathrm{HF}}}{n_l - n_k} = \sum_r n_r\big(\langle kr|lr\rangle - \langle kr|rl\rangle\big)$$

$$v_{kk}^{\mathrm{HF}} = \frac{\partial W^{\mathrm{HF}}}{\partial n_k} = \sum_r n_r\big(\langle kr|lr\rangle - \langle kr|rl\rangle\big)$$

Derivation of the Fock potential

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Derivation of the Fock potential

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$$\forall_{k\neq l} \qquad v_{kl}^{\mathrm{HF}} = \frac{W_{kl}^{\mathrm{HF}\dagger} - W_{kl}^{\mathrm{HF}}}{n_l - n_k} = \sum_r n_r\big(\langle kr|lr\rangle - \langle kr|rl\rangle\big)$$

$$v_{kk}^{\mathrm{HF}} = \frac{\partial W^{\mathrm{HF}}}{\partial n_k} = \sum_r n_r\big(\langle kr|lr\rangle - \langle kr|rl\rangle\big)$$

$$\Rightarrow \qquad v_{kl}^{\mathrm{HF}} = \sum_r n_r\big(\langle kr|lr\rangle - \langle kr|rl\rangle\big) \quad \Rightarrow h_{kl} + v_{kl}^{\mathrm{HF}} = f_{kl}$$

DFT

$$W^{\text{DFT}} = E_{Hxc}[\rho] \qquad \rho(\boldsymbol{x}) = \sum_k n_k |\phi_k(\boldsymbol{x})|^2$$

DFT

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DFT

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$$W_{kl}^{\mathrm{DFT}} = \int \mathrm{d}\boldsymbol{x}\, \frac{\partial W^{\mathrm{DFT}}}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) = \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{x}'\, \frac{\delta W^{\mathrm{DFT}}}{\delta \rho(\boldsymbol{x}')} \frac{\partial \rho(\boldsymbol{x}')}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x})$$

DFT

$$W^{\text{DFT}} = E_{Hxc}[\rho] \qquad \rho(\boldsymbol{x}) = \sum_k n_k |\phi_k(\boldsymbol{x})|^2$$

$$\begin{aligned} W_{kl}^{\text{DFT}} &= \int \mathrm{d}\boldsymbol{x} \, \frac{\partial W^{\text{DFT}}}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) = \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{x}' \, \frac{\delta W^{\text{DFT}}}{\delta \rho(\boldsymbol{x}')} \frac{\partial \rho(\boldsymbol{x}')}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) \\ &= \int \mathrm{d}\boldsymbol{x} \, \frac{\delta E_{Hxc}}{\delta \rho(\boldsymbol{x})} n_k \phi_k^*(\boldsymbol{x}) \phi_l(\boldsymbol{x}) \end{aligned}$$

DFT

$$W^{\mathrm{DFT}} = E_{Hxc}[\rho] \qquad\qquad \rho(\boldsymbol{x}) = \sum_k n_k |\phi_k(\boldsymbol{x})|^2$$

$$\begin{aligned} W_{kl}^{\mathrm{DFT}} &= \int \mathrm{d}\boldsymbol{x}\, \frac{\partial W^{\mathrm{DFT}}}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) = \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{x}'\, \frac{\delta W^{\mathrm{DFT}}}{\delta \rho(\boldsymbol{x}')} \frac{\partial \rho(\boldsymbol{x}')}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) \\ &= \int \mathrm{d}\boldsymbol{x}\, \frac{\delta E_{Hxc}}{\delta \rho(\boldsymbol{x})} n_k \phi_k^*(\boldsymbol{x}) \phi_l(\boldsymbol{x}) = n_k \int \mathrm{d}\boldsymbol{x}\, \phi_k^*(\boldsymbol{x}) v^{Hxc}(\boldsymbol{x}) \phi_l(\boldsymbol{x}) \end{aligned}$$

DFT

$$W^{\mathrm{DFT}} = E_{Hxc}[\rho] \qquad\qquad \rho(\boldsymbol{x}) = \sum_k n_k |\phi_k(\boldsymbol{x})|^2$$

$$\begin{aligned} W_{kl}^{\mathrm{DFT}} &= \int \mathrm{d}\boldsymbol{x}\, \frac{\partial W^{\mathrm{DFT}}}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) = \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{x}'\, \frac{\delta W^{\mathrm{DFT}}}{\delta \rho(\boldsymbol{x}')} \frac{\partial \rho(\boldsymbol{x}')}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) \\ &= \int \mathrm{d}\boldsymbol{x}\, \frac{\delta E_{Hxc}}{\delta \rho(\boldsymbol{x})} n_k \phi_k^*(\boldsymbol{x}) \phi_l(\boldsymbol{x}) = n_k \int \mathrm{d}\boldsymbol{x}\, \phi_k^*(\boldsymbol{x}) v^{Hxc}(\boldsymbol{x}) \phi_l(\boldsymbol{x}) = n_k v_{kl}^{Hxc} \end{aligned}$$

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$$W^{\mathrm{DFT}} = E_{Hxc}[\rho] \qquad\qquad \rho(\boldsymbol{x}) = \sum_k n_k |\phi_k(\boldsymbol{x})|^2$$

$$\begin{aligned} W_{kl}^{\mathrm{DFT}} &= \int \mathrm{d}\boldsymbol{x}\, \frac{\partial W^{\mathrm{DFT}}}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) = \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{x}'\, \frac{\delta W^{\mathrm{DFT}}}{\delta \rho(\boldsymbol{x}')} \frac{\partial \rho(\boldsymbol{x}')}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) \\ &= \int \mathrm{d}\boldsymbol{x}\, \frac{\delta E_{Hxc}}{\delta \rho(\boldsymbol{x})} n_k \phi_k^*(\boldsymbol{x}) \phi_l(\boldsymbol{x}) = n_k \int \mathrm{d}\boldsymbol{x}\, \phi_k^*(\boldsymbol{x}) v^{Hxc}(\boldsymbol{x}) \phi_l(\boldsymbol{x}) = n_k v_{kl}^{Hxc} \\ W_{kl}^{\mathrm{DFT}\dagger} &= W_{lk}^{\mathrm{DFT}*} \end{aligned}$$

DFT

$$W^{\text{DFT}} = E_{Hxc}[\rho] \qquad\qquad \rho(\boldsymbol{x}) = \sum_k n_k |\phi_k(\boldsymbol{x})|^2$$

$$\begin{aligned}
W_{kl}^{\text{DFT}} &= \int \mathrm{d}\boldsymbol{x}\, \frac{\partial W^{\text{DFT}}}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) = \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{x}'\, \frac{\delta W^{\text{DFT}}}{\delta \rho(\boldsymbol{x}')} \frac{\partial \rho(\boldsymbol{x}')}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) \\
&= \int \mathrm{d}\boldsymbol{x}\, \frac{\delta E_{Hxc}}{\delta \rho(\boldsymbol{x})} n_k \phi_k^*(\boldsymbol{x}) \phi_l(\boldsymbol{x}) = n_k \int \mathrm{d}\boldsymbol{x}\, \phi_k^*(\boldsymbol{x}) v^{Hxc}(\boldsymbol{x}) \phi_l(\boldsymbol{x}) = n_k v_{kl}^{Hxc} \\
W_{kl}^{\text{DFT}\dagger} &= W_{lk}^{\text{DFT}*} = n_l v_{kl}^{Hxc}
\end{aligned}$$

DFT

$$W^{\text{DFT}} = E_{Hxc}[\rho] \qquad \rho(\boldsymbol{x}) = \sum_k n_k |\phi_k(\boldsymbol{x})|^2$$

$$\begin{aligned} W_{kl}^{\text{DFT}} &= \int \mathrm{d}\boldsymbol{x}\, \frac{\partial W^{\text{DFT}}}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) = \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{x}'\, \frac{\delta W^{\text{DFT}}}{\delta \rho(\boldsymbol{x}')} \frac{\partial \rho(\boldsymbol{x}')}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) \\ &= \int \mathrm{d}\boldsymbol{x}\, \frac{\delta E_{Hxc}}{\delta \rho(\boldsymbol{x})} n_k \phi_k^*(\boldsymbol{x}) \phi_l(\boldsymbol{x}) = n_k \int \mathrm{d}\boldsymbol{x}\, \phi_k^*(\boldsymbol{x}) v^{Hxc}(\boldsymbol{x}) \phi_l(\boldsymbol{x}) = n_k v_{kl}^{Hxc} \\ W_{kl}^{\text{DFT}\dagger} &= W_{lk}^{\text{DFT}*} = n_l v_{kl}^{Hxc} \end{aligned}$$

$$\forall_{k \neq l} \qquad v_{kl}^{\text{DFT}}$$

DFT

$$W^{\mathrm{DFT}} = E_{Hxc}[\rho] \qquad\qquad \rho(\boldsymbol{x}) = \sum_k n_k |\phi_k(\boldsymbol{x})|^2$$

$$\begin{aligned}
W_{kl}^{\mathrm{DFT}} &= \int \mathrm{d}\boldsymbol{x}\, \frac{\partial W^{\mathrm{DFT}}}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) = \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{x}'\, \frac{\delta W^{\mathrm{DFT}}}{\delta \rho(\boldsymbol{x}')} \frac{\partial \rho(\boldsymbol{x}')}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) \\
&= \int \mathrm{d}\boldsymbol{x}\, \frac{\delta E_{Hxc}}{\delta \rho(\boldsymbol{x})} n_k \phi_k^*(\boldsymbol{x}) \phi_l(\boldsymbol{x}) = n_k \int \mathrm{d}\boldsymbol{x}\, \phi_k^*(\boldsymbol{x}) v^{Hxc}(\boldsymbol{x}) \phi_l(\boldsymbol{x}) = n_k v_{kl}^{Hxc} \\
W_{kl}^{\mathrm{DFT}\dagger} &= W_{lk}^{\mathrm{DFT}*} = n_l v_{kl}^{Hxc}
\end{aligned}$$

$$\forall_{k \neq l} \qquad v_{kl}^{\mathrm{DFT}} = \frac{W_{kl}^{\mathrm{DFT}\dagger} - W_{kl}^{\mathrm{DFT}}}{n_l - n_k}$$

DFT

$$W^{\mathrm{DFT}} = E_{Hxc}[\rho] \qquad\qquad \rho(\boldsymbol{x}) = \sum_k n_k |\phi_k(\boldsymbol{x})|^2$$

$$\begin{aligned}
W^{\mathrm{DFT}}_{kl} &= \int \mathrm{d}\boldsymbol{x}\, \frac{\partial W^{\mathrm{DFT}}}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) = \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{x}'\, \frac{\delta W^{\mathrm{DFT}}}{\delta \rho(\boldsymbol{x}')} \frac{\partial \rho(\boldsymbol{x}')}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) \\
&= \int \mathrm{d}\boldsymbol{x}\, \frac{\delta E_{Hxc}}{\delta \rho(\boldsymbol{x})} n_k \phi_k^*(\boldsymbol{x}) \phi_l(\boldsymbol{x}) = n_k \int \mathrm{d}\boldsymbol{x}\, \phi_k^*(\boldsymbol{x}) v^{Hxc}(\boldsymbol{x}) \phi_l(\boldsymbol{x}) = n_k v^{Hxc}_{kl} \\
W^{\mathrm{DFT}\dagger}_{kl} &= W^{\mathrm{DFT}*}_{lk} = n_l v^{Hxc}_{kl}
\end{aligned}$$

$$\forall_{k \neq l} \qquad v^{\mathrm{DFT}}_{kl} = \frac{W^{\mathrm{DFT}\dagger}_{kl} - W^{\mathrm{DFT}}_{kl}}{n_l - n_k} = v^{Hxc}_{kl}$$

DFT

$$W^{\mathrm{DFT}} = E_{Hxc}[\rho] \qquad\qquad \rho(\boldsymbol{x}) = \sum_k n_k |\phi_k(\boldsymbol{x})|^2$$

$$\forall_{k\neq l} \qquad v_{kl}^{\mathrm{DFT}} = \frac{W_{kl}^{\mathrm{DFT}\dagger} - W_{kl}^{\mathrm{DFT}}}{n_l - n_k} = v_{kl}^{Hxc}$$

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$$\forall_{k \neq l} \qquad v_{kl}^{\mathrm{DFT}} = \frac{W_{kl}^{\mathrm{DFT}\dagger} - W_{kl}^{\mathrm{DFT}}}{n_l - n_k} = v_{kl}^{Hxc}$$

$$v_{kk}^{\mathrm{DFT}} = \frac{\partial W^{\mathrm{DFT}}}{\partial n_k}$$

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$$v_{kk}^{\mathrm{DFT}} = \frac{\partial W^{\mathrm{DFT}}}{\partial n_k} = \int \mathrm{d}\boldsymbol{x} \, \frac{\delta E_{Hxc}}{\delta \rho(\boldsymbol{x})} \frac{\partial \rho(\boldsymbol{x})}{\partial n_k}$$

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$$W^{\text{DFT}} = E_{Hxc}[\rho] \qquad \rho(\boldsymbol{x}) = \sum_k n_k |\phi_k(\boldsymbol{x})|^2$$

$$\forall_{k\neq l} \qquad v_{kl}^{\text{DFT}} = \frac{W_{kl}^{\text{DFT}\dagger} - W_{kl}^{\text{DFT}}}{n_l - n_k} = v_{kl}^{Hxc}$$

$$v_{kk}^{\text{DFT}} = \frac{\partial W^{\text{DFT}}}{\partial n_k} = \int \mathrm{d}\boldsymbol{x}\, \frac{\delta E_{Hxc}}{\delta \rho(\boldsymbol{x})} \frac{\partial \rho(\boldsymbol{x})}{\partial n_k}$$

$$= \int \mathrm{d}\boldsymbol{x}\, \phi_k^*(\boldsymbol{x}) v^{Hxc}(\boldsymbol{x}) \phi_k(\boldsymbol{x})$$

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$$\forall_{k\neq l} \qquad v_{kl}^{\text{DFT}} = \frac{W_{kl}^{\text{DFT}\dagger} - W_{kl}^{\text{DFT}}}{n_l - n_k} = v_{kl}^{Hxc}$$

$$v_{kk}^{\text{DFT}} = \frac{\partial W^{\text{DFT}}}{\partial n_k} = \int \mathrm{d}\boldsymbol{x}\, \frac{\delta E_{Hxc}}{\delta\rho(\boldsymbol{x})} \frac{\partial \rho(\boldsymbol{x})}{\partial n_k}$$

$$= \int \mathrm{d}\boldsymbol{x}\, \phi_k^*(\boldsymbol{x}) v^{Hxc}(\boldsymbol{x}) \phi_k(\boldsymbol{x}) = v_{kk}^{Hxc}$$

DFT

$$W^{\text{DFT}} = E_{Hxc}[\rho] \qquad\qquad \rho(\boldsymbol{x}) = \sum_k n_k |\phi_k(\boldsymbol{x})|^2$$

$$\forall_{k \neq l} \qquad v_{kl}^{\text{DFT}} = \frac{W_{kl}^{\text{DFT}\dagger} - W_{kl}^{\text{DFT}}}{n_l - n_k} = v_{kl}^{Hxc}$$

$$v_{kk}^{\text{DFT}} = \frac{\partial W^{\text{DFT}}}{\partial n_k} = \int \mathrm{d}\boldsymbol{x}\, \frac{\delta E_{Hxc}}{\delta \rho(\boldsymbol{x})} \frac{\partial \rho(\boldsymbol{x})}{\partial n_k}$$

$$= \int \mathrm{d}\boldsymbol{x}\, \phi_k^*(\boldsymbol{x}) v^{Hxc}(\boldsymbol{x}) \phi_k(\boldsymbol{x}) = v_{kk}^{Hxc}$$

$$\Rightarrow \qquad v_{kl}^{\text{DFT}} = v_{kl}^{Hxc}$$

DFT

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$$v_{kl}^{\mathrm{1MFT}} = \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{x}'\, \phi_k^*(\boldsymbol{x}) \frac{\delta W}{\delta\gamma(\boldsymbol{x}', \boldsymbol{x})} \phi_l(\boldsymbol{x}')$$

full derivation

Conclusions

- Karush–Kuhn–Tucker (KKT) conditions: Lagrange multipliers for inequality constraints

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- Karush–Kuhn–Tucker (KKT) conditions: Lagrange multipliers for inequality constraints
- Derivation of Aufbau
- Unified derivation of effective one-electron equations for HF, DFT and 1MFT

Extra's

Hartree-Fock

The HF functional again

$$W^{\mathrm{HF}}[\{\phi\},\{n\}] = \frac{1}{2}\sum_{rs} n_r n_s w_{rssr} - \frac{1}{2}\sum_{rs} n_r n_s w_{rsrs}$$

Hartree-Fock

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Also valid for fractional occupation numbers?

The HF functional again

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Also valid for fractional occupation numbers?
Lieb showed that $E^{\mathrm{HF}} \geq \langle \Phi_0 | \hat{H} | \Phi_0 \rangle$

$$\Phi_0(\boldsymbol{x}_1,\dots,\boldsymbol{x}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(\boldsymbol{x}_1) & \dots & \phi_1(\boldsymbol{x}_N) \\ \vdots & \ddots & \vdots \\ \phi_N(\boldsymbol{x}_1) & \dots & \phi_N(\boldsymbol{x}_N) \end{vmatrix}$$

1MFT

$$W^{\text{1MFT}} = W[\gamma] \qquad \gamma(\boldsymbol{x}, \boldsymbol{x}') = \sum_k n_k \phi_k(\boldsymbol{x}) \phi_k^*(\boldsymbol{x}')$$

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$$\begin{aligned} W_{kl}^{\text{1MFT}} &= \int \mathrm{d}\boldsymbol{x}\, \frac{\partial W}{\partial \phi_k(\boldsymbol{x})}\phi_l(\boldsymbol{x}) = \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{y} \int \mathrm{d}\boldsymbol{y}'\, \frac{\delta W}{\delta\gamma(\boldsymbol{y},\boldsymbol{y}')} \frac{\partial\gamma(\boldsymbol{y},\boldsymbol{y}')}{\partial\phi_k(\boldsymbol{x})}\phi_l(\boldsymbol{x}) \\ &= \int \mathrm{d}\boldsymbol{y} \int \mathrm{d}\boldsymbol{y}'\, \frac{\delta W}{\delta\gamma(\boldsymbol{y},\boldsymbol{y}')} n_k \phi_k^*(\boldsymbol{y}')\phi_l(\boldsymbol{y}) \end{aligned}$$

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&= \int \mathrm{d}\boldsymbol{y} \int \mathrm{d}\boldsymbol{y}'\, \frac{\delta W}{\delta\gamma(\boldsymbol{y},\boldsymbol{y}')} n_k \phi_k^*(\boldsymbol{y}')\phi_l(\boldsymbol{y}) \\
&= n_k \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{x}'\, \phi_k^*(\boldsymbol{x}) \frac{\delta W}{\delta\gamma(\boldsymbol{x}',\boldsymbol{x})}\phi_l(\boldsymbol{x}')
\end{aligned}$$

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W_{kl}^{1\text{MFT}\dagger} &= W_{lk}^{1\text{MFT}*}
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\end{aligned}$$

$\forall_{k \neq l} \qquad v_{kl}^{\text{1MFT}}$

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back